ELSEVIER
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Procedia Engineering
Volume 143, 2016, Pages 1252–1259
Advances in Transportation Geotechnics 3 . The 3rd International Conference on Transportation Geotechnics (ICTG 2016)
Procedia Engineering

Nanotechnology Applied to Chemical Soil Stabilization

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Abstract
The chemical stabilization of a soil is dependent on a wide range of parameters, being the most important ones associated to the soil properties and cementitious materials. The mechanical behavior of a soil can be improved with addition of nanoparticles, which are not a cementitious material but once introduced in a soil they are expected to reduce the interparticles' spacing and nanoreinforce it. This will promote the construction of a stronger and stiffer soil skeleton matrix together with the cementitious materials. However, to maximize the benefits of the nanoparticles added to a stabilized soil it is crucial to overcome the problems related with particle agglomeration. Thus, it was defined a screening strategy which comprises the characterization of the nanoparticles, the definition of the aqueous medium with surfactant addition, the characterization of the surfactant and the application of energy to promote the particles' dispersion. The quality of the suspension, in terms of particles' dispersion, was evaluated trough the analysis of the particle size distribution given by dynamic light scattering (DLS). After, a series of performance tests with cement Portland and nanoparticles were conducted. The results from the unconfined compressive strength (UCS) tests have shown the high potential of adding multiwall carbon nanotubes to a chemically stabilized soil. The results have also pointed out the importance of the nanoparticles dispersion process.

Keywords: Carbon nanotubes; Soil stabilization; Unconfined compressive strength

1 Introduction

The increasing growth of urban and metropolitan areas over the world demands construction in coastal and lowland regions, in many cases geologically characterized by poor geotechnical properties (low strength and high compressibility). This is a major issue for many transportation geotechnics applications. To overcome these difficulties, it is usual to adopt ground improvement techniques, being the chemical stabilization one of the techniques that have been used with success in practice (Correia et al. 2015, Lorenzo and Bergado 2004, Porbaha 1998).

Selection and peer-review under responsibility of the Scientific Programme Committee of ICTG 2016

doi:10.1016/j.proeng.2016.06.113

The chemical stabilization technique consists in the mechanical mixing of the natural soil with cementitious materials in order to improve its mechanical behaviour. In general, the characteristics of the soil are difficult to change at the site, so, the subsequent study focus namely on the impact that cementitious materials have on the mechanical behaviour of the stabilized soil. The cementitious materials used in practice are, in the majority of cases, Portland cement (Porbaha 1998, Kitazume and Terashi 2013). However, it is common the replacement of part of the Portland cement by additives (Edil and Staab 2005, Kitazume and Terashi 2013) specifically adapted to the soil requirements, resulting in technical and economic advantages. Among the different types of additives that can be used in chemical stabilization of soils, this work gives special emphasis to additives consisting of nanoparticles, more precisely to multiwall carbon nanotubes (MWCNTs). MWCNTs exhibit unique physical properties, including ultrahigh specific surface, extremely high yield strength and moduli of elasticity, and elastic behaviour, all pointing out to the potential of MWCNTs in reinforcing applications (Makar 2011). In addition, the introduction of such nanoscale particles in the cementitious material has the potential to affect both the physical structure and the chemical reactions occurring during cement curing. The MWCNTs are not a cementitious material but once introduced in a soil they are expected to reduce the interparticles' spacing and nanoreinforce it, which will promote the construction of a stronger and stiffer soil skeleton matrix, together with the cementitious materials, therefore improving the mechanical properties of the soil. The greatest challenge for the application of MWCNTs as an additive in soil stabilization is associated with its natural tendency to aggregate, resulting in the loss of its beneficial properties. To overcome this problem it is common the use of surfactants and/or ultrasonic energy to promote dispersion of the nanoparticles in suspension. The use of ultrasounds should be minimized because it is an energy-inefficient technique, thus the use of surfactants can help in minimizing ultrasounds requirement.

This work is focused on the application of MWCNTs on soil stabilization, evaluating its applicability in terms of the quality of the dispersion of the suspension and of the mechanical behaviour of the new composite material. For this purpose two surfactants, with different molecular weight and charge were chosen (Glycerox and Amber 4001). The choice was to evaluate the influence of molecular weight and charge on the quality of the dispersion. The two surfactants were fully characterized before being used to disperse the MWCNTs. The characterization relied on light scattering techniques, including Dynamic and Static Light Scattering (DLS and SLS) and Electrophoretic Light Scattering (ELS). Finally, the dispersions of nanoparticles were added to the main agent responsible for soil stabilization, the Portland cement, and the mechanical behaviour of the stabilized soil was studied by unconfined compressive strength (UCS) tests.

2 Materials and Experimental Procedure

2.1 Materials

Table 1 presents the geotechnical and chemical properties of the Coimbra soft soil (located in a region known as "Baixo Mondego" near Coimbra city, Portugal), used in the study. In general, the soil is mostly composed of silt with some clay and sand particles, with a high organic matter content (9.3%), which has a strong influence on some characteristics of the soil, namely, low unit weight (14.6 kNm^3), high plasticity, high natural water content (80.9%), high void ratio, low strength and high compressibility (Coelho 2000, Correia 2011). The chemical composition of the soft soil (Table 1) reveals a high content of silica (SiO_2) and alumina (Al_2O_3), which confers pozzolanic properties to the soil. Therefore, in the long term it can react with calcium hydroxide producing strength-enhancing reaction products (Taylor 1997, Janz and Johansson 2002). The soil exhibits a reduced value of pH, which can restrain and/or delay some reactions during the chemical stabilization (Correia 2011, Kitazume and Terashi 2013). A more detailed description and characterization of the soil can be found in Correia (2011), Casaleiro (2014) and Figueiredo (2014).

Property	
w_{nat} (%)	80
γ_{sat} (kN/m3)	14.6
e_{nat} (-)	2.1
Clay fraction (%)	8-12
Silt fraction (%)	71
Sand fraction (%)	17-21
G (-)	2.55
OM (%)	9.3
w_L (%)	71
w_P (%)	43

Chemical compound	
CaO (%)	0.74
SiO_2 (%)	62
Al_2O_3 (%)	16
Fe_2O_3 (%)	4.8
MgO (%)	1.1
K_2O (%)	3
pH (-)	3.5

Table 1: Main properties of the Coimbra soft soil.

The binder selected to chemically stabilize the soil was a Portland cement type I, class of mechanical resistance 42.5 (CEM I 42,5 R), with a chemical composition in terms of the main constituents given in Table 2. The cement particles have a specific surface of 349.0 m^2/kg and are negatively charged (zeta potential measured was -2.14 mV). The quantity of Portland cement used for the chemical stabilization of the soil was 175 kg/m^3.

CaO (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MgO (%)	SO_3	Specific surface (m^2/kg)
63	19	5	3	2,5	3.35	349

Table 2: Composition and specific surface of the binder.

The carbon nanotubes selected were multiwall carbon nanotubes (MWCNTs) which is justified by its cost (100.000€/ton) lower than the single-wall carbon nanotubes. The MWCNTs were produced by Nanocyl and, according to their data, the CN7000 has an average diameter of 9.5 nm, average length of 1500 nm and a specific surface about 1 000 times higher than cement particles. MWCNTs are composed essentially of pure carbon (90%), with some metal oxides (10%). Further characterization of the MWCNTs was conducted with the assessment of the mass density (1.7 g/cm^3) and zeta potential (-25.2 mV, evaluated by ELS).

In this study two surfactants were studied as additives to promote the dispersion of the MWCNTs. The surfactant Amber 4001 was a 'tailored' surfactant, produced, supplied and protected by legal rights by the company AQUATECH from Switzerland. It is classified as an amphoteric surfactant, cationic at low pH (measured by ELS), having a molecular weight of 54.2 kDa (evaluated by SLS) and surfactant molecule size of 5.6 nm (Z-average is a measure of the diameter evaluated by DLS). The Glycerox is a commercial surfactant which is produced by the company Lubrizol. It is classified as a non-ionic surfactant, having a molecular weight of 4265 kDa (evaluated by SLS) and surfactant molecule size of 41.9 nm (Z-average is a measure of the diameter evaluated by DLS). More details about properties of the surfactants may be found in Figueiredo (2014) and Figueiredo et al (2015).

2.2 Experimental Procedure

The experimental procedure adopted is based on two tests types: size distribution using DLS to assess the quality of the dispersion of MWCNT in an aqueous medium; and unconfined compressive strength (UCS) tests in order to evaluate the mechanical performance of the soil chemically stabilized with a binder which incorporates MWCNT "properly" dispersed in an aqueous medium, either pure water or a solution of surfactant.

The method tested in this work to demonstrate the applicability of MWCNT dispersions consists in the addition of the MWCNT to an aqueous medium and subsequent application of ultrasonic energy (power of 500W, frequency of 20 kHz, time equal to 5 minutes). The tests were made for a concentration of MWCNT of 0.001% (referred to the dry weight of cement), combined with a surfactant concentration of 0.5, 1, 2 and 3% (weight percentage in water). Each suspension produced was finally characterized by DLS. A detailed description of the laboratory procedure followed for the evaluation of the dispersions quality is presented in Figueiredo (2014) and Correia et al (2015).

Finally, performance tests were done to characterize the mechanical behavior of the soil stabilized with a binder enriched with MWCNT. The experimental procedure involved the following steps (a more detailed description is found in Figueiredo 2014, Correia et al 2015):

- Homogenization of soil: the soil stored was re-moved from the thermo-hygrometric chamber and was homogenized manually. It was taken the soil mass necessary to prepare two samples. The initial water content of the soil was con-trolled.
- Mixing: the Portland cement (on a quantity of 175 kg/m^3) was blended in a beaker with 150 mL of suspension (water or aqueous solution of surfactant + MWCNT). Then this mixture was put into the mixing bowl with soil. It was used a mechanical mixer (Hobart N50) at a rate of 136 rpm. The mixture was homogenized during three minutes. After complete mixing, a small portion of the mixture was withdrawn to assess the water content post-blending. The sample must be introduced in the mold straight away up to a maximum time of 30 minutes after mixing was stopped, otherwise there is a risk of the sample becoming a hard mass.
- Compression: It was used cylindrical molds made from PVC pipes with inner diameter of 37 mm and height of 325 mm; in the inner surface of the mold, vaseline was smeared in order to promote the sample slide; at the base of the mold it was glued duct tape and a circular geotextile filter so that the sample does not come out of the mold. The samples were introduced in the mold in 6 layers. For each layer, a slight compression was applied with a circular plate followed by application of vibration with the help of a hand drill to eliminate air bubbles within the mixture, followed by new slight compression. This process has always been applied to all 6 layers. In the end a new circular geotextile filter was applied to the top of the sample.
- Curing: the molds with fresh samples were placed in a vertical position on a curing tank filled with water at a temperature of 20 ± 2°C. During the curing period a vertical pressure of 24 kPa was applied at the top of each sample, in order to simulate actual field vertical effective stress at a depth of 5 m (Correia 2011). The curing time for all samples was 7 days.
- Extraction of sample: the molds were taken from the curing tank and the samples were demolded using a hydraulic extractor. The specimens were carefully cut so that they had a height of 76 mm and a height/diameter ratio of 2. The specimen was weighed for evaluation of the density.
- UCS test: the sample is placed on the testing machine and subjected to unconfined compression at a constant deformation rate of 1%/min in relation to the height of the sample. During the test, the force applied to the sample was automatically registered as a function of the vertical displacement of the sample. After failure, the sample was removed from the test machine and the final water content was measured.

A reference test where just water was added to Portland cement was made. As surfactants can promote not only the dispersion of MWCNT but also the dispersion of the particles of soil and cement, tests only with each surfactant and cement were performed as well. The nomenclature adopted for the tests is a sum of a letter (G or A for an aqueous solution with the surfactant Glycerox or Amber 4001, respectively) followed by a number specifying the surfactant concentration, plus the letters CNT if the MWCNTs are present. For each different test conditions, at least two samples were tested. They were only validated if the range of variation of the maximum strength was within the interval defined by the average ± 15%.

3 Results

Table 3 summarizes all results. The quality of the MWCNT dispersions are expressed by the Z-average value (MWCNT's diameter evaluated by DLS) of the suspensions, while the mechanical behavior performance is characterized by two parameters measured from the stress-strain results: the maximum unconfined compressive strength ($q_{u\,max}$) and the secant undrained Young's modulus at 50% of the $q_{u\,max}$, E_{u50}.

Test nomenclature	DLS Test	UCS test	
	Z-average (nm)	$q_{u\,max}$ (kPa)	E_{u50} (MPa)
Reference test	-	143	15.8
A0.5	-	176.5	31.5
A1	-	206	31.9
A2	-	115.5	20.7
A3	-	97.5	9.2
G3	-	181.4	34.6
A0.5CNT	521.4	225	36
A1CNT	322.8	237.5	38.7
A2CNT	-	158	18.6
A3CNT	316.8	131	9.9
G3CNT	155.1	190.5	23.8

Table 3: Summary of results (average values). Portland cement quantity = 175 kg/m^3; MWCNTs concentration = 0.001%.

Figure 1 presents the stress-strain plots from UCS tests regarding the samples prepared only with water, i.e., that do not incorporate MWCNTs (for a better clarity of results, only one of the samples of each test condition is represented in the figure). The results indicate that for the surfactant Amber 4001, concentrations up to 1% has a beneficial effect in terms of mechanical properties. However, for higher concentrations it seems that there are too many molecules of surfactant, which instead of adsorbing on the surface of the soil and cement particles to promote their dispersion, may start to form micelles, which in such a medium with large particles can make the hydration reactions between cement and water more difficult decreasing the mechanical performance of the final samples. This explanation is compatible with the "good" dispersion obtained for a concentration of 3% (low Z-average value) for Amber 4001 and Glycerox, since the formation of micelles is not necessarily detrimental for MWCNT particles dispersion (Figure 2). It should be stated that DLS tests were done in a medium where MWCNT were mixed only with the aqueous solution of surfactant, while for the UCS tests, these dispersions were placed in a totally different environment where, besides the soil particles, there were also cement particles reacting chemically with water.

The results also point out that the addition of a small quantity of MWCNT leads to further mechanical improvement as showed in Table 3 and Figure 3. This effect is explained by the nanodimensions of MWCNTs, filling the "larger" voids of the soil-cement matrix, so the composite material becomes denser, stronger and stiffer.

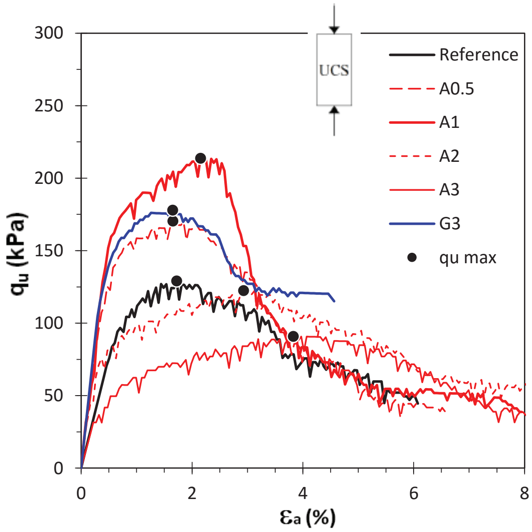

Figure 1: Stress-strain plots (UCS tests without MWCNT).

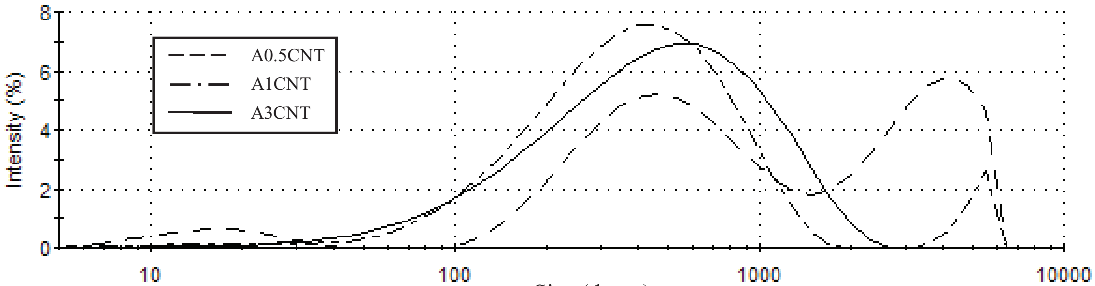

Figure 2: Size distribution by intensity (DLS test).

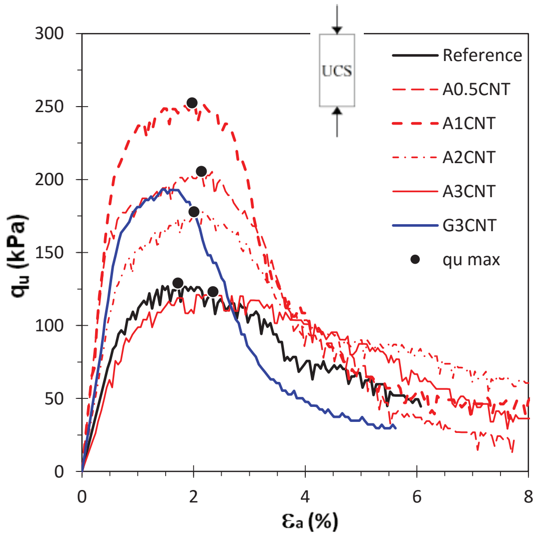

Figure 3: Stress-strain plots (UCS tests with MWCNT).

4 Conclusions

The results have shown that the presence of nanoparticles in a soil-cement matrix has the ability to reduce the interparticles' spacing and nanoreinforce the soil, which will promote the construction of a stronger and stiffer soil skeleton matrix together with the cementitious materials, therefore improving the mechanical properties of the material. The mechanical enhancement can be increased if the quality of the MWCNT dispersion improves, which can be obtained by adding a surfactant to the solution. The maximum beneficial improvement reached was of the order of 66.1% and 144.9%, respectively for the $q_{u\,max}$ and E_{u50}, when referred to the reference test without MWCNT.

The results also showed that the addition of the surfactant alone may have the ability to disperse the cement particles, as proved by the beneficial effects obtained for concentrations of Amber 4001 up to 1%. The good dispersion of the cement particles will thus lead to a better filling of void spaces between soil particles building a solid matrix even more resistant.

The combination of the effects associated to the incorporation of MWCNT with the presence of surfactant is not a superposition of effects (direct sum) as stated in Table 3 and Figures 1 and 3, due to the interdependence between both effects (Correia et al. 2015; Figueiredo et al 2015).

Acknowledgements

The authors would like to express their thanks to CIMPOR and AQUATECH for supplying the binder and the surfactants, respectively, to *Instituto Pedro Nunes* that kindly provided the probe-sonicator used and to the institutions that supported the research financially: University of Coimbra, CIEPQPF, ACIV, FCT through the project PEst/C/EQB/UI0102/2013 and *MAIS CENTRO InovC* Ignition Grant/2014.

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